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Leaching and Selected Hydraulic Properties of Processed Oil Shales

Colorado State Univ., Fort Collins

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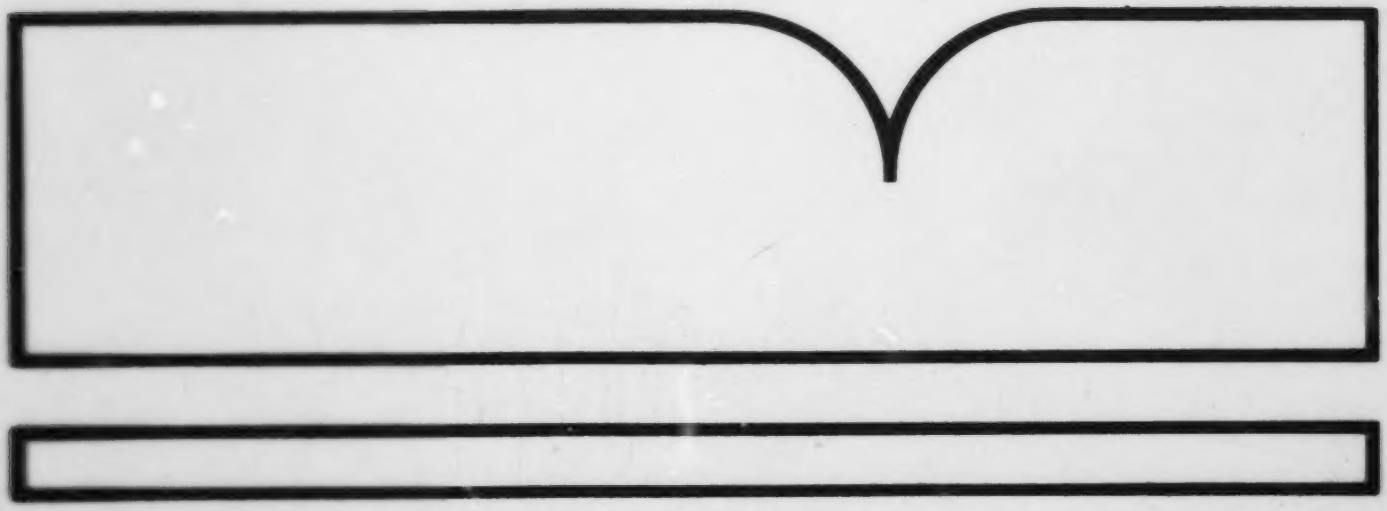

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16. ABSTRACT

This report describes a column leaching test procedure developed to simulate the leaching of high volume wastes under semi-arid field conditions. The report also present results obtained when retorted oil shales (Tosco, Paraho, Lurgi) are leached by this procedure. Selected hydraulic properties are also discussed for these retorted shales including permeability and water holding capacity.

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ENVIRONMENTAL RESEARCH BRIEF

Leaching and Selected Hydraulic Properties of Processed Oil Shales

David B. McWhorter and Victor A. Nazareth*

Introduction

This research brief presents selected data on the leaching and hydraulic properties of processed oil shales. More complete descriptions of the methodology and analysis, as well as additional data, and descriptions of the materials tested, are available in two other, more comprehensive documents listed at the end of this research brief.

A characteristic feature of field leachate generation is the invasion of a leachant into a body of porous medium that may already contain some moisture. The antecedent moisture content (that moisture existing prior to invasion) may range from practically 0% to perhaps 20% by weight. The chemical composition of the leachate will be strongly dependent upon the chemical composition of the antecedent moisture. The chemistry of the antecedent moisture, in turn, should reflect chemical equilibrium achieved at small liquid-to-solid ratios ranging up to approximately 0.20. The results of laboratory column tests, designed to simulate this salient feature of field leachate generation, are presented herein. In addition, the results of measurements of the capillary water-holding capacity and hydraulic conductivity at the satiated water content are reported.

The ESM Test Procedure

The ESM (Equilibrated Soluble Mass) test consists of displacement of an equilibrated antecedent solution by a leachant. In all of the tests reported herein, distilled water was used as both the moisturizing solution and the leachant.

The test was conducted by injecting distilled water at a constant rate into the bottom of the vertical column (shown in Figure 1). The diameter of the vertical column was 10 cm and the length of the test section was 30 cm. The bottom and top end fixtures were constructed with a slight concavity to assure that liquid entered and exited the porous medium uniformly over the cross-section. The perforated plate on the bottom served to supportthe retorted shale. An ordinary milk filter between the porous medium and the perforated plates on the top and bottom prevented the movement of fines.

The leachant was injected by a positive displacement pump so that a constant injection rate could be maintained under the conditions of variable pumping head that prevailed prior to the beginning of effluent production. Effluent from the top of the column was routed through an electrical conductivity probe into a graduated cylinder. A record was maintained of the cumulative volume of effluent as a function of time. The effluent was sampled frequently and subjected to chemical analysis. In most instances, the sample volume represented 1% or less of the pore volume of the packed column so the sample could be regarded as a point sample.

The packed column was prepared by first thoroughly mixing the test material then rolling it out on a plastic sheet. The sample was then quartered and one quarter was spread over a second plastic sheet. A spray bottle was used to add

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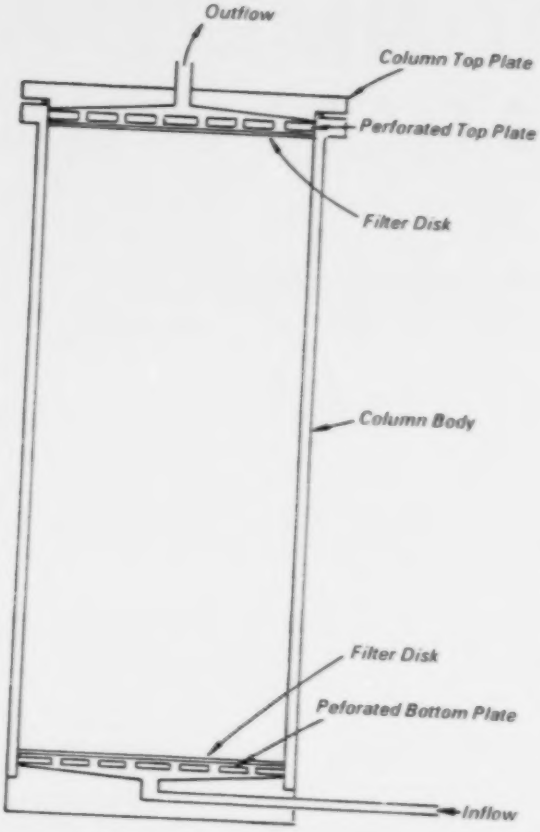

Figure 1. Schematic diagram of leaching column.

distilled water to the material while mixing was maintained. When the desired water content was reached, the moist sample was placed in a double plastic bag and closed. An equilibration time of 24 hrs was allowed before the material was placed in the column.

The empty column together with end fixtures, support plates, and filters was weighed. The column was then packed with the moist retorted shale and weighed again. A sample of the moist shale was weighed, oven dried, and weighed again to determine the antecedent moisture content of the packed column. Material was added to the column through a funnel attached to a rigid, hollow stem that extended to the bottom of the column. Material entered the column through the stem on a short upstroke and was compacted by impact of the stem on the downstroke. This method prevented a particle segregation by free fall and prompted a uniform packing. Additional compaction was achieved by impacting the column on a rubber mat.

From a mathematical analysis (Nazareth, 1984; McWhorter and Nazareth, 1984), it was concluded that the first effluent from columns prepared and injected (as described above) is comprised entirely of antecedent moisture provided that

$$\frac{\theta_i L^{1/2}}{\theta_m} >> \frac{1}{2}\left(\frac{D}{V_m}\right)^{1/2}$$

where

θ_i = antecedent volumetric water content

θ_m = satiated water content

L = length of column

V_m = seepage velocity at satiated water content

D = coefficient of hydrodynamic dispersion at the satiated water content.

Thus, the test provides a means of measuring the chemical composition of the antecedent moisture that has been equilibrated with the solid at a liquid-to-solid ratio corresponding to that expected in the field. Provided that the above condition is satisfied, the chemistry of the initial effluent is independent of column length, a very important conclusion relative to conducting laboratory tests. Furthermore, the conclusion that antecedent moisture is displaced by the invading liquid applies to the field situation, as well. In other words, the first leachage generated in the field is expected to be undiluted antecedent moisture.The ESM test provides a method for assessing the chemical composition of antecedent moisture which has equilibrated with the solid under conditions reasonably similar to field conditions.

ESM Test Results

Table 1 contains the values of the experimental parameters for four ESM tests. Runs 33 and 34 served as replicates to test for reproducibility. Tables 2 through 5 present the concentrations of several species in the column effluent (leachate). Initially, the effluent from the LURGI retorted shale columns is a sodium-sulfate water which becomes a calcium-sulfate water near the end of the tests. The effluent from the TOSCO II retorted shale columns remains a sodium-sulfate water throughout the test. The data suggest the presence of abundant solid phase calcium-sulfate in the LURGI retorted shale but not in the TOSCO II retorted shale. Fluoride concentrations in the effluent from the LURGI columns were readily reduced by leaching, in contrast to the nearly constant levels of fluoride observed in TOSCO II effluent. The concentrations of molybdenum were reduced by leaching in both materials, but the levels were much greater in the TOSCO II effluent.

Figures 2, 3, and 4 indicate the degree to which the ESM test is reproducible. Excellent agreement between the two tests is indicated by the EC curves and the chloride curves. The breakthrough curves for sulfate show a great deal more scatter but they, too, are in general agreement. Table 6 presents data on several trace elements observed in the effluent from the LURGI retorted shale.

Table 1. Summary of Test Parameters for ESM Leach Tests

Material	LURGI ULG		TOSCO II	
Run No.	33	34	29	35
Packed Length, L(cm)	29.8	29.8	30.0	29.8
Cross-Section Area, A(cm^2)	80.12	80.12	80.12	80.12
Bulk Density, ρ_b (g/cm^3)	1.609	1.606	1.187	1.269
Porosity, Φ	0.404	0.405	0.554	0.512
Initial liquid content, θ_i	0.159	0.162	0.142	0.188
Max. liquid content, θ_m	0.354	0.345	0.470	0.450
Inflow Darcy flux, q_o (cm/h)	0.857	0.861	0.946	0.999

Table 2. Effluent Concentrations for Run No. 33 (LURGI ULG)

Cum V ml	EC-25°C dS/m	F	Cl	SO_4	Na mg/L	Ca	Mg	Mo
11.5	15.81	17.8	355	9,650	3,830	519	0.619	5.53
84.5	15.81	13.8	329	9,620	3,820	446	0.444	5.74
152.9	15.91	11.6	329	10,940	3,530	450	0.367	5.27
221.1	15.71	10.9	336	9,760	3,780	469	0.419	5.46
300.7	14.52	9.65	289	8,870	3,380	507	0.381	3.30
368.8	12.03	9.44	236	7,160	2,450	503	0.383	3.48
436.5	9.47	8.52	176	5,200	1,850	514	0.427	1.93
504.5	7.36	7.72	84.9	4,060	1,090	536	0.430	0.758
584.7	5.59	6.66	79.1	2,980	659	565	0.455	1.59
653.3	4.71	7.29	63.4	2,560	413	560	0.479	0.674
727.7	4.18	6.34	36.6	2,290	400	576	0.393	0.395
797.9	3.91	5.57	28.3	2,130	239	637	0.422	0.724
1121.7	3.48	5.00	14.4	2,010	151	619	0.561	<0.05

Cum V = cumulative volume of leachate.
EC-25°C = electrical conductivity standardized at 25°C.

Table 3. Effluent Concentrations for Run No. 34 (LURGI ULG)

Cum V ml	EC-25°C. dS/m	F	Cl	SO_4	Na mg/L	Ca	Mg	Mo
12.4	14.91	13.0	341	9,840	3,680	466	0.478	7.24
83.9	14.81	12.5	250	10,000	3,830	469	0.558	9.02
156.4	15.50	11.7	326	8,180	3,780	483	0.487	7.46
227.1	15.40	11.0	326	8,080	3,770	477	0.449	5.60
309.9	14.09	10.0	296	7,050	3,400	490	0.394	6.44
380.2	11.04	8.73	217	6,410	2,630	460	0.482	5.57
451.0	8.26	6.95	140	4,730	1,500	518	0.518	2.27
520.4	6.44	6.19	88.3	3,900	1,170	554	0.554	2.06
600.3	5.11	10.8	-----	2,160	604	565	0.550	1.02
668.8	4.51	4.83	84.8	2,130	498	383	0.616	0.884
738.0	4.17	6.14	41.9	2,440	312	576	0.649	<0.05
806.2	3.88	4.75	22.1	1,990	215	584	0.712	----
1105.6	3.73	4.24	8.08	2,100	126	597	0.756	0.446

Cum V = cumulative volume of leachate.
EC- 25°C.= electrical conductivity standardized at 25°C.

Table 4. Effluent Concentrations for Run No. 29 (TOSCO III)

Cum V ml	Lab. EC dS/m	F	Cl	SO_4	Na mg/L	Ca	Mg	Mo
49.1	38.90	29.2	-----	23,300	-----	397	483	56.4
85.1	38.90	-----	217	-----	12,700	368	536	59.1
133.1	38.80	27.6	270	10,830	12,200	328	-----	57.6
198.9	36.00	27.9	251	30,180	1[illegible],400	373	498	49.3
259.4	3.60	26.0	193	27,070	9,620	332	457	15.3
348.9	23.60	22.8	115	6,840	7,000	371	329	10.4
449.5	14.50	22.1	48.2	11,580	6,660	354	233	6.56
587.8	8.58	20.3	24.2	5,710	896	285	151	3.71
781.2	4.28	22.2	9.88	2,370	664	154	76.8	2.28
980.1	2.70	26.3	9.02	1,420	448	59.8	40.8	1.62
1106.0	2.30	28.9	8.21	1,050	-----	44.5	32.0	1.45

Cum V = cumulative volume of leachate.
Lab. EC = electrical conductivity measured directly from test effluent.

Table 5. Effluent Concentrations for Run No. 35 (TOSCO III)

Cum V ml	Lab EC dS/m	F	Cl	SO_4	Na mg/L	Ca	Mg	K	Mo
12.4	36.50	24.9	218	28,510	9,910	368	695	109	26.3
76.5	36.50	23.6	211	28,380	10,430	342	687	108	26.0
141.4	36.50	20.1	212	30,530	10,300	322	680	125	26.0
205.9	36.40	31.7	204	29,670	10,160	348	696	162	26.0
273.0	36.20	23.3	208	27,410	10,100	354	687	136	25.8
337.9	32.90	20.3	191	20,380	8,850	318	599	91.5	24.2
413.0	24.70	20.6	105	16,450	6,380	274	416	86.6	19.2
489.7	17.80	20.9	52.8	9,761	3,670	169	260	43.8	13.2
565.2	12.20	22.0	24.1	7,141	2,470	112	164	30.6	9.44
640.7	8.77	20.1	12.1	5,120	1,750	79.5	116	23.5	6.97
716.0	6.62	22.0	8.93	3,132	1,160	61.7	83.3	15.4	5.36
791.6	5.29	23.7	6.32	2,513	968	49.7	73.6	14.8	4.20
865.9	4.26	25.1	5.49	2,046	772	40.6	56.0	11.7	3.29
938.5	3.68	26.0	4.69	1,685	678	34.9	47.2	11.9	2.99
1113.7	2.60	28.3	4.52	1,097	436	22.3	35.5	7.66	2.29
1233.6	2.23	29.2	3.89	965	371	15.7	33.2	5.84	1.73

Cum V = cumulative volume of leachate.
Lab. EC = electrical conductivity measured directly from test effluent.

Hydraulic Properties

The hydraulic part of the research includes the determination of the capillary water-holding capacity and the permeability at the satiated water content for several processed shales, in keeping with the aim of this continuing research to provide complete data on hydraulic properties as functions of water content, including the dry range in which vapor transport is dominant.

The procedure for measurement of the hydraulic conductivity at saturation is that given in Designation E-13 in the USBR Earth Manual. This is a constant head test using an 8-inch diameter permeameter. A schematic of the experimental apparatus is shown in Figure 5. This setup shown, permits the simulation of overburden load by application of a load to the top plate.

The procedure first selects the dry bulk density at which the permeability is desired. In commercial operations, the materials are placed in the disposal piles at a moisture content determined by the amount of water required for compaction, cooling, and dust control. A sample of the material is then brought to the prescribed moisture content using standard procedures, and weighing out the quantity of material required to achieve the specified dry density. This quantity of material is then packed in the permeameter in either four 1-in. lifts or, in the case of the PARAHO material, in 2-in. lifts to form a test thickness of 4 in.

Packing of the permeameter is accomplished using the standard weight hammer. In the case of the PARAHO material, the sample is packed inside an inner sleeve that raises as the material is packed. In the annular space

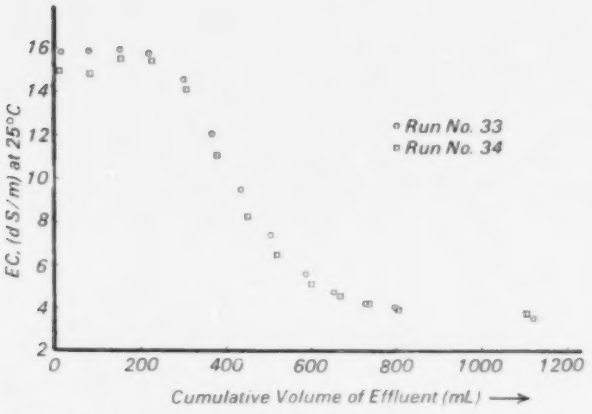

Figure 2. *Electrical conductivity of LURGI ULG effluent samples.*

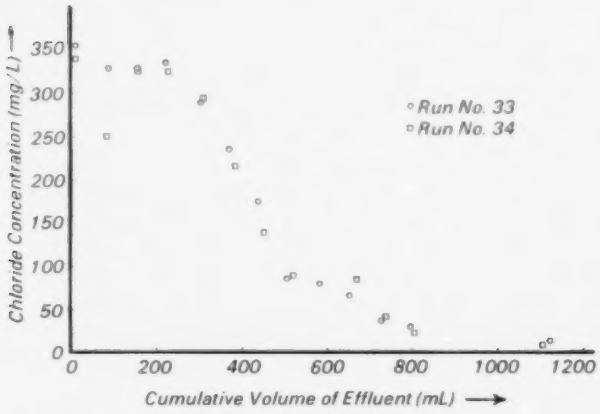

Figure 3. *Chloride concentration in LURGI ULG effluent samples.*

between the inner cylinder and the wall of the permeameter, minus 10 material is vigorously packed, to prevent channeling adjacent to the wall, a situation most likely to occur with the coarse grained PARAHO residue.

After packing is complete, the top plates are put in place and the simulated overburden load is applied, using a hydraulic jack. A load cell is attached to an extension of the shaft of the jack and is calibrated to indicate the total force applied. The desired force is maintained by a large spring compressed during the loading. When the jack is removed, the material in the permeameter is slowly saturated by upward flow. A gradient of about unity is maintained during saturation to minimize the possibility of piping. The permeability is measured as a function of time periods up to one week or more. Flow rates through the sample are determined from a calibrated Mariotte siphon that also maintains a constant head on the inflow side.

The dry bulk densities to be tested may range from a minimum of about 1.3 g/cm³ (81 lb/ft³) to the maximum Standard Proctor density. Measurement of permeability at

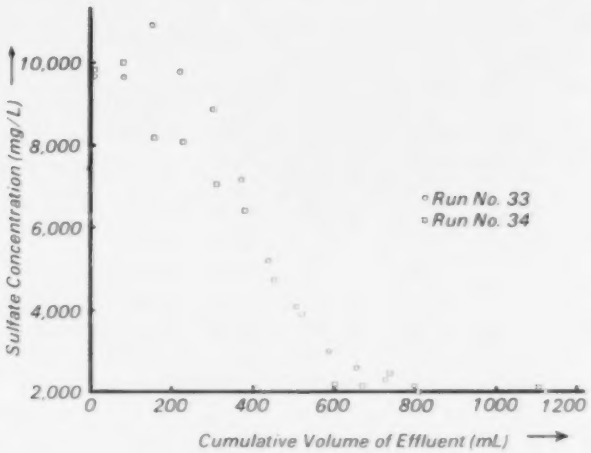

Figure 4. *Sulfate concentration in LURGI ULG effluent samples.*

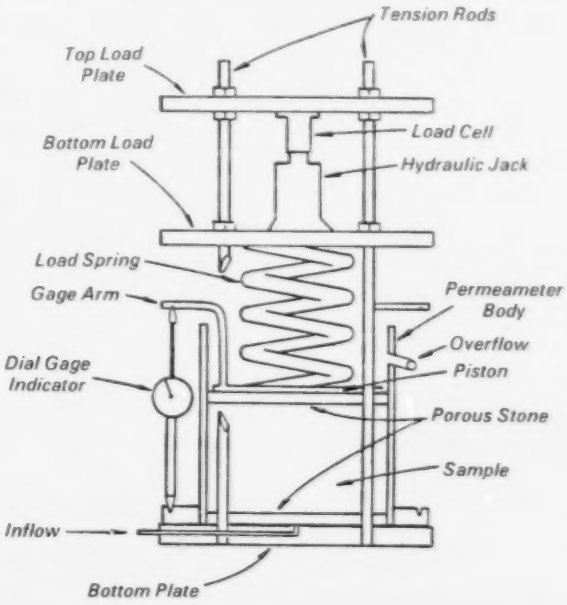

Figure 5. *Schematic of permeameter.*

the maximum Standard Proctor density is made on samples packed in the permeameter at a moisture content corresponding to the maximum Standard Proctor density.

The results of the hydraulic conductivity measurements are summarized in Table 7, with the lowest values on the order of 10^{-7} cm/s, or of the same order as expected average net-infiltration rates.

Capillary Water Holding Capacities

The water retention characteristics of the retorted shale residues on hand are being measured. Duplicate 25 g shale

Table 6. Trace Element Concentrations in Effluent from LURGI Retorted Shale (Run 34)

Cum V ml	B	Be	Si	Mn	Al	Ba	Sr	Li	Fe	Cd	Pb	As
						mg/L						
12.4	1.31	0.091	14.8	0.047	4.48	0.140	14.4	1.31				
83.9	1.05	0.017	12.5	0.061	3.87	0.142	16.1	1.14	0.06	<0.01	<0.1	0.1
156.4	0.86	0.019	15.0	0.039	3.87	0.142	16.3	1.11				
227.1	0.43	0.009	10.7	-----	3.55	0.121	13.3	1.12				
309.9	0.72	0.024	14.4	0.020	4.00	0.132	15.2	1.10	0.05	<0.01	<0.1	0.1
380.2	0.42	-----	13.1	0.026	3.77	0.154	14.6	1.10				
451.0	0.45	-----	12.2	0.023	2.66	0.108	13.2	1.12				
520.4	0.37	0.034	13.6	0.037	2.66	0.122	14.5	1.10				
600.3	0.37	0.021	12.3	0.020	2.27	0.116	15.1	1.07	0.05	<0.01	<0.1	<0.1
668.8	0.55	0.058	11.7	0.060	2.57	0.105	13.9	1.03				
738.0	0.48	0.042	9.7	0.033	1.98	0.090	11.3	1.00				
806.2	-----	-----	-----	-----	-----	-----	-----	0.88				
1105.6	0.11	0.005	19.1	0.019	2.50	0.176	14.4	0.83	0.06	<0.01	<0.1	<0.1

Table 7. Summary of Hydraulic Conductivity Measurements (cm/s)

Material	Moisture Content %	Packed Dry Density gm/cm³	Method	Load (psi) 50	100	200
			Constant Head	6.85×10^{-6}	6.15×10^{-6}	5.65×10^{-6}
TOSCO II	21.0	1.56	Falling Head	6.0×10^{-6}	4.9×10^{-6}	4.97×10^{-6}
		1.39	Constant Head	5.6×10^{-5}	4.6×10^{-5}	3.90×10^{-5}
Proctor Results	11.0	1.39	Falling Head	5.2×10^{-5}	5.2×10^{-5}	3.23×10^{-5}
Optimum Moisture Content: 19.5%		1.29	Constant Head	6.7×10^{-5}	4.0×10^{-5}	2.45×10^{-5}
Proctor Density: 1.57 gm/cm³	11.0	1.29	Falling Head	6.7×10^{-5}	4.34×10^{-5}	2.69×10^{-5}
LURGI RG 1	26.7	1.40	Falling Head	1.0×10^{-6}	6.5×10^{-7}	6.5×10^{-7}
		1.33	Constant Head	3.0×10^{-5}	1.9×10^{-5}	1.9×10^{-5}
Proctor Results	10.5	1.33	Falling Head	2.8×10^{-5}	1.4×10^{-5}	1.9×10^{-5}
Optimum Moisture Content: 30%		1.2	Constant Head	1.4×10^{-5}	1.32×10^{-5}	1.28×10^{-5}
Proctor Density: 1.4 gm/cm³	10.0	1.2	Falling Head	8.5×10^{-6}		
		1.7	Constant Head	4.7×10^{-7}	4.2×10^{-7}	4.5×10^{-7}
PARAHO	20.0	1.7	Falling Head	5.0×10^{-7}	4.6×10^{-7}	4.0×10^{-7}
		1.7	Constant Head	1.9×10^{-6}	1.3×10^{-6}	1.3×10^{-7}
Proctor Results	20.0	1.7	Falling Head	8.1×10^{-7}	8.1×10^{-7}	7.8×10^{-7}
Optimum Moisture Content: 20%		1.36	Constant Head	9.8×10^{-4}	7.0×10^{-4}	2.4×10^{-4}
Proctor Density: 104 pcf (1.7 gm/cm³)	10.0	1.36	Falling Head	9.8×10^{-4}		
		1.7	Constant Head	1.9×10^{-5}	$1,5 \times 10^{-5}$	1.0×10^{-5}
HYTORT	18.0	1.7	Falling Head			
Proctor Results	10.0	1.5	Constant Head	3.4×10^{-3}	2.5×10^{-3}	2.5×10^{-3}
Optimum Moisture Content: 20%						
Proctor Density: 104 pcf (1.7 gm/cm³)						

samples are wetted to approximately 20% by weight and packed to a specified dry bulk density. These samples are saturated and placed in contact with a saturated porous ceramic plate (bubbling pressure = 15 atm) which, in turn is placed in a pressure chamber. The base of the ceramic plate is covered by a rubber bladder that is sealed to the circumference of the plate. The space between the base of the plate and the bladder is connected to the atmosphere through a drain line that exits from the pressure chamber.

After the saturated samples are placed on the ceramic plate, and the plate put in the pressure chamber, a specified

Table 8. Moisture Contents* of Processed Shales at Various Pressure and Bulk Densities

Sample	Pressure 14.7 psi (1 bar)	44.1 psi (3 bar)	73.5 psi (5 bar)	147 psi (10 bar)	200 psi (13.6 bar)
No Compaction					
Lurgi Ash	73.6	62.0	64.5	63.1	59.5
TOSCO II	48.0	45.8	45.9	43.8	44.7
Lurgi	27.5	27.6	26.9	25.3	15.5
Packed to a BD = 1.30 g/cc					
Lurgi Ash	62.4	62.3	62.2	62.0	61.7
TOSCO	42.2	42.0	41.9	41.6	41.4
HYTORT	35.2	33.7	32.6	31.8	31.0
BD = 1.45 g/cc					
Lurgi Ash	60.2	58.7	56.6	55.5	55.2
TOSCO	36.0	33.8	32.9	32.1	30.5
HYTORT	31.0	27.6	25.3	23.8	23.2
BD = 1.60 g/cc					
Lurgi Ash	47.2	46.3	45.8	44.4	43.7
TOSCO	34.6	33.5	32.1	30.8	30.5
HYTORT	30.5	30.3	28.9	25.4	24.6
Lurgi	20.7	20.2	19.8	19.8	19.0

*Table entries are moisture contents (w) expressed on a weight % basis: weight of water per unit weight of dry solids.

air pressure is created within the chamber. The excess air pressure displaces a portion of the water contained in samples. This water passes from the sample through the plate and out the drain line. Air is prevented from entering the region between the bladder and the plate because the saturated ceramic has no permeability to air. The specified air pressure in the chamber is maintained until drainage ceases (usually about 24 hrs), at which time the pressure is released and the samples are weighed to determine the water content corresponding to the applied pressure.

The samples are replaced on the plate and a higher air pressure is again exerted. An additional increment of water is displaced and the samples are again weighed. This process is continued until the desired range of determinations are completed. In the set of experiments completed to date, the range of pressures utilized is 1 to 14 atmospheres. The results of the water holding tests are contained in Table 8.

References

Nazareth, V. A. 1984. A Laboratory Column Leach Test for Oil Shale Solid Wastes. Ph. D. Dissertation, Colorado State Univ., Fort Collins, CO, 130 p.

McWhorter, D. B. and Nazareth, V. A. 1984. Leaching of Processed Oil Shales. Progress Report, Cooperative Agreement CR-807668, Colorado State Univ., Fort Collins, CO, 60 p.